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## MODELLING OF CATION RETENTION IN ION CHROMATOGRAPHY USING FIXED-SITE AND DYNAMICALLY COATED ION-EXCHANGE COLUMNS

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### SUMMARY

A retention model is derived for inorganic cations eluted from cation-exchange columns with eluents containing a single competing cation and a complexing ligand. This model is evaluated using divalent solute cations and a low-capacity fixed-site cation-exchange column, and good agreement is obtained between theoretical and experimental results both for simple cation exchange and also when complexation effects are present. Sodium ions added to the eluent during pH adjustment were found to contribute significantly to the elution of solute cations and should be included in all calculations using the retention model. Retention characteristics were also studied for an ion-interaction chromatographic system using a C<sub>18</sub> column, octanesulfonic acid as the ion-interaction reagent, and oxalate as the complexing ligand in the eluent. Experimental data for this system did not show close agreement with the ion-exchange retention model. Discrepancies are attributed to variations in the ion-exchange capacity of the dynamically coated ion-exchange column during the study. However, qualitative agreement with the ion-exchange retention model was obtained when the concentration of octanesulfonate in the eluent was varied.

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### INTRODUCTION

Theoretical models which describe the manner in which solute retention varies with changing eluent composition in ion chromatography (IC) are of fundamental importance to the understanding of solute retention mechanisms. Moreover, valid models provide an essential basis for selection of the best eluent composition to effect a desired separation, whether this selection be performed on a trial-and-error basis, or with the aid of a computer optimization procedure<sup>1</sup>.

Since the inception of IC, a large volume of research has been directed towards the development of a retention model which describes accurately the retention of anionic solutes. In situations where the eluent contains only a single competing anion, a relatively straightforward retention model can be derived which gives good agreement with experimental measurements<sup>2-5</sup>. However, complications arise when

the eluent contains two or more competing anions, such as phthalate eluents in non-suppressed IC and carbonate-bicarbonate eluents in suppressed IC. It has been demonstrated that in these cases, all eluent species must be considered if reliable retention modelling is to be attained<sup>6,7</sup>. This generally involves the calculation of ion-exchange selectivity coefficients for each solute anion with each eluent anion and is therefore a time-consuming process.

The study of retention models for inorganic cations has been much more limited than is the case for anions. In separation systems which involve purely ion exchange, cations are usually eluted with an eluent containing a single competing cation, such as hydrogen ions or ethylenediammonium ions<sup>8</sup>. In many cases however, complexing agents are also added to the eluent in order to accelerate the elution of cations or to modify the selectivity which can be attained by ion exchange alone<sup>9,10</sup>. It is also common for cation separations to be performed by ion-interaction chromatography using dynamically coated columns<sup>11</sup>. In this paper we develop a retention model which is potentially applicable to each of these situations. The validity of this model is then examined for both low-capacity fixed-site ion-exchange columns (as used in IC separations) and for ion-interaction separations. One aim of this study has been to evaluate whether a retention model suitable for fixed-site cation exchangers can be applied successfully to the dynamically-coated type of ion-exchangers used in ion-interaction chromatography.

## THEORY

### *Ion-exchange with a single eluent competing cation*

We begin by considering the simplest case in cation-exchange IC, in which the eluent contains a single type of competing cation. The ion-exchange equilibrium for binding of a solute cation,  $M^{x+}$ , to a stationary phase which has been conditioned with an eluent containing a competing cation,  $E^{y+}$ , is given by:



where the subscripts m and r refer to the mobile and resin phases, respectively. Fig. 1a shows a schematic representation of this ion-exchange equilibrium and it can be seen

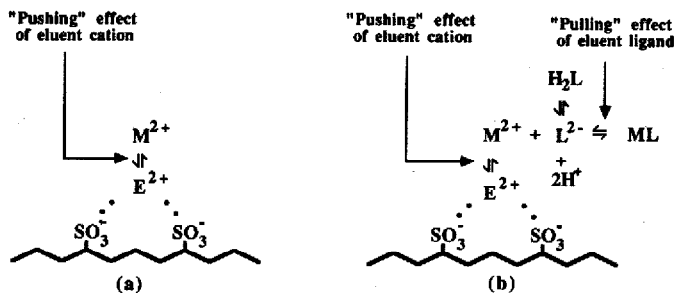


Fig. 1. Schematic representation of the elution of a solute  $M^{2+}$  from a sulfonic acid cation exchanger by (a) simple cation exchange with a single competing cation ( $E^{2+}$ ) and (b) cation exchange with a competing cation and a complexing ligand ( $L^{2-}$ ) in the eluent.

that the eluent competing cation exerts a “pushing” effect on the solute cation, which is responsible for elution of that solute. If activity coefficients are assumed to be equal to unity, the selectivity coefficient,  $K_{M,E}$  can be written:

$$K_{M,E} = \frac{[M_r^{x+}]^y [E_m^{y+}]^x}{[M_m^{x+}]^y [E_r^{y+}]^x} \tag{2}$$

The weight distribution coefficient for solute M is designated as  $D_M$  and is given by:

$$D_M = \frac{[M_r^{x+}]}{[M_m^{x+}]} \tag{3}$$

In general, the weight diffusion coefficient is related to the capacity factor ( $k'_M$ ) for solute  $M^{x+}$  by the expression

$$k'_M = D_M \frac{w}{V_m} \tag{4}$$

where  $w$  is the weight of the stationary phase and  $V_m$  is the volume of mobile phase. From eqns. 3 and 4 we obtain:

$$\frac{[M_r^{x+}]}{[M_m^{x+}]} = k'_M \frac{V_m}{w} \tag{5}$$

Substituting into eqn. 2 gives:

$$K_{M,E} = \left( k'_M \frac{V_m}{w} \right)^y \left( \frac{[E_m^{y+}]}{[E_r^{y+}]} \right)^x \tag{6}$$

If we assume that the eluent ion,  $E^{y+}$ , occupies  $y$  ion-exchange sites on the stationary phase, then the ion-exchange capacity of the column,  $Q$ , is given by:

$$[E_r^{y+}] = \frac{Q}{y} \tag{7}$$

Eqn. 6 now becomes:

$$K_{M,E} = \left( k'_M \frac{V_m}{w} \right)^y \left( \frac{Q}{y} \right)^{-x} [E_m^{y+}]^x \tag{8}$$

which can be rearranged to give:

$$k'_M = \frac{w}{V_m} (K_{M,E})^{\frac{1}{y}} \left( \frac{Q}{y} \right)^{\frac{x}{y}} [E_m^{y+}]^{-\frac{x}{y}} \tag{9}$$

When expressed in logarithmic form, eqn. 9 becomes:

$$\log k'_M = \frac{1}{y} \log K_{M,E} + \frac{x}{y} \log \frac{Q}{y} + \log \frac{w}{V_m} - \frac{x}{y} \log [E_m^{y+}] \quad (10)$$

Eqn. 10 is of fundamental importance to ion chromatography and allows the following predictions to be made for the situation in which only a single type of competing cation is present in the eluent:

(i) When a solute cation  $M^{x+}$  is eluted with a competing cation  $E^{y+}$ , eqn. 10 shows that the capacity factor for  $M^{x+}$  is determined by the selectivity coefficient  $K_{M,E}$ , the ion-exchange capacity of the column,  $Q$ , the ratio of stationary to mobile phases,  $w/V_m$ , and the concentration of competing cations in the eluent,  $[E_m^{y+}]$ . Increases in  $K_{M,E}$ ,  $Q$  or  $w/V_m$  lead to increased capacity factors, whilst increasing  $[E_m^{y+}]$  leads to decreased capacity factors.

(ii) Increased eluent charge leads to decreased capacity factors, whilst increased solute charge leads to increased capacity factors.

(iii) Under conditions where the same solute cation,  $M^{x+}$  is chromatographed on the same column with varying concentrations of competing cation ( $E^{y+}$ ) in the eluent, then eqn. 10 predicts that a plot of  $\log k'_M$  versus  $\log [E_m^{y+}]$  will be a straight line of slope equal to  $-x/y$ .

#### *Cation exchange with complexing eluents*

The simple cation-exchange retention model described above can be extended to include an eluent component which participates in complexation reactions with solute cations. When a solute cation,  $M^{x+}$ , is eluted by a competing cation,  $E^{y+}$ , and the eluent also contains  $H_2L$ , where  $L^{2-}$  is a ligand capable of reacting with  $M^{x+}$ , we have the situation depicted in Fig. 1b. Under these conditions, the equilibrium shown in eqn. 1 applies, but we must also consider the further equilibria shown in eqns. 11–14:



We can define  $\alpha_M$  as the fraction of the total concentration of metal ion in the eluent which is present in the free form, *i.e.* as  $M^{x+}$ :

$$\alpha_M = \frac{[M_m^{x+}]}{[M_m^{x+}] + [ML_m^{x-2}] + [ML_2^{x-4}]} = \frac{[M_m^{x+}]}{C_M} \quad (15)$$

where  $C_M$  is the total concentration of metal ion in the mobile phase, regardless of the form in which it is present.  $C_M$  is given by:

$$C_M = [M_m^{x+}] + [ML_m^{x-2}] + [ML_2^{x-4}] \quad (16)$$

Assuming that  $M^{x+}$  is the only form of the metal which is bound to the cation-exchange resin (*i.e.* the complexes formed with  $L^{2-}$  are either neutral or anionic), then the distribution coefficient for solute  $M^{x+}$  can be defined as:

$$D_M = \frac{[M_r^{x+}]}{C_M} \tag{17}$$

Substituting eqns. 15 and 17 into eqn. 2 gives:

$$K_{M,E} = \frac{(D_M)^y [E_m^{y+}]^x}{(\alpha_M)^y [E_r^{y+}]^x} \tag{18}$$

If we now substitute eqns. 4 and 7, we obtain:

$$k'_M = \frac{\alpha_M^w}{V_m} (K_{M,E})^{\frac{1}{y}} \left(\frac{Q}{y}\right)^{\frac{x}{y}} [E_m^{y+}]^{-\frac{x}{y}} \tag{19}$$

which can be presented in logarithmic form as:

$$\log k'_M = \log \alpha_M + \frac{1}{y} \log K_{M,E} + \frac{x}{y} \log \frac{Q}{y} + \log \frac{w}{V_m} - \frac{x}{y} \log [E_m^{y+}] \tag{20}$$

If we now consider only the case of a divalent metal cation ( $x = 2$ ), and we assign equilibrium constants of  $K_{a1}$ ,  $K_{a2}$ , (*i.e.* acid dissociation constants) to eqns. 11 and 12, and  $K_1$  and  $K_2$  (stepwise formation constants) to eqns. 13 and 14, then  $\alpha_M$  is given by:

$$\alpha_M = \frac{1}{1 + K_1 \alpha_L C_L + K_1 K_2 \alpha_L C_L^2} \tag{21}$$

where  $C_L$  is the total concentration of ligand species in the eluent, and  $\alpha_L$  is the fraction of  $C_L$  which exists as  $L^{2-}$ .  $\alpha_L$  is given by:

$$\alpha_L = \frac{[L_m^{2-}]}{[L_m^{2-}] + [HL_m^-] + [H_2L_m]} = \frac{K_{a1} K_{a2}}{[H_m^+]^2 + K_{a1}[H_m^+] + K_{a1} K_{a2}} \tag{22}$$

Eqn. 20 applies to both of the cation-exchange separation mechanisms depicted in Fig. 1. When no complexing ligand is present,  $\alpha_M$  is equal to unity and eqn. 20 reduces to eqn. 10. Under conditions where the column and the nature of the eluent and solute ions are constant, eqn. 20 can be simplified to:

$$\log k'_M = \log \alpha_M - \frac{x}{y} \log [E_m^{y+}] + \text{constant} \tag{23}$$

## EXPERIMENTAL

*Instrumentation*

Two liquid chromatographic instruments were used, each being dedicated to a specific separation mode. Studies with a fixed-site ion-exchange column were performed using a Millipore-Waters (Milford, MA, U.S.A.) Model M45 pump fitted with a pulse dampener, U6K injector, and a Model 430 conductivity detector interfaced to a Houston instruments (Austin, TX, U.S.A.) Omniscribe chart recorder. The column was housed in a Millipore-Waters column heater Model 1122/WTC-120. The instrumentation employed for ion-interaction separations consisted of a Millipore-Waters Model 510 pump fitted with a pulse dampener, U6K injector, Model 481 variable-wavelength UV-VIS detector interfaced to an Omniscribe dual-pen chart recorder. Post-column reaction detection of eluted metal ions was achieved through the use of a Millipore-Waters reagent delivery module, operated at pressures in the range 5.9 to 6.2 bar.

*Columns*

A Millipore-Waters  $\mu$ Bondapak C<sub>18</sub> column (300 × 3.9 mm I.D.) packed with 10- $\mu$ m particles was used for the ion-interaction separations. Chromatography using fixed-site ion exchange was performed on a Millipore-Waters TSK gel IC PAK Cation SW (50 × 4.6 mm I.D.) column packed with 5- $\mu$ m sulfonated silica gel, with an ion-exchange capacity of 450 ± 15  $\mu$ equiv./g. The  $\mu$ -Bondapak column was operated at ambient temperature whilst the IC PAK Cation SW column was maintained at 35°C. Both columns were operated at a flow-rate of 1.0 ml/min.

*Reagents and procedures*

Eluent solutions were prepared from malic acid, glacial acetic acid (BDH, Poole, U.K.), oxalic acid, nitric acid (Ajax, Sydney, Australia), tartaric acid, sodium hydroxide (May and Baker, Australia), and sodium 1-octanesulfonate (Aldrich, Milwaukee, WI, U.S.A.). The post-column reagent was prepared from 4-(2-pyridyl-azo)-resorcinol monosodium monohydrate (PAR reagent), ammonia gas and ascorbic acid (Merck, Darmstadt, F.R.G.). All reagents were analytical grade and were used without further purification, except for the nitric acid which was distilled in a PTFE still.

Standard solutions of metal ions were made by dissolving spectroscopically pure metals or metal oxides in hydrochloric or nitric acids, and diluting to volume using polypropylene volumetric ware. Water treated with a Millipore (Bedford, MA, U.S.A.) Milli-Q water purification system was used to prepare the eluents and standard solutions. The pH of each eluent was adjusted with solid sodium hydroxide and dilute nitric acid, and eluents were filtered through a 0.45- $\mu$ m membrane filter and then degassed in an ultrasonic bath prior to use.

The post-column reagent solution was prepared by dissolving 0.02 g PAR in 105 ml 15 M aqueous ammonia and 35 ml glacial acetic acid, followed by dilution to 500 ml. The aqueous ammonia component of the post-column reagent solution was prepared by bubbling ammonia gas through water and measuring the specific gravity to determine concentration.

## RESULTS AND DISCUSSION

*Single eluent competing cation*

Eqn. 20 predicts a linear relationship between the logarithm of the concentration of the eluent competing cation ( $\log [E_m^{z+}]$ ) and the logarithm of the solute capacity factor ( $\log k'_M$ ), with a negative slope given by the ratio of charges on the solute and eluent cations (*i.e.*  $x/y$ ). This relationship has been examined by a number of authors<sup>8,12,13</sup>. Elution of monovalent cations using nitric acid eluents showed good agreement with theory, with all solutes giving linear plots of slopes in the range  $-1.06$  to  $-1.13$  (ref. 12). Sevenich and Fritz<sup>14</sup> have studied the retention of divalent and trivalent cations on a low-capacity (0.06 mequiv./g) cation-exchanger using perchloric acid eluents. Linear retention plots were observed only when activity effects were considered; that is, when  $\log k'_M$  was plotted against  $\log (HClO_4)$ , where the parentheses indicate activity. Table I summarizes some of the slopes obtained in this study for divalent and trivalent cations.

Agreement between the slopes obtained experimentally and those predicted from eqn. 20 is generally good, although there are some exceptions. It can be noted that these slopes provide information on the effective charge on the metal ion. Lederer<sup>13</sup> has recently reviewed much of the literature relating to the determination of the effective charge on a metal ion (or metal complex ion) using ion-exchange methods, and has concluded:

(i) Activity effects are of importance, especially for polyvalent cations and when the eluent strength is high. Complete correction for activity effects requires knowledge not only of the activity coefficient of the competing cation in the eluent phase, but also of the activity coefficients for metal ion in the eluent phase and the metal ion and the competing cation in the resin phase. Most of these coefficients are not available. Neglecting activity effects will tend to produce slopes which are smaller than those predicted from eqn. 20.

(ii) For some cations the effective charge is reduced due to steric effects which prevent the cation interacting with a stoichiometric number of functional groups on

TABLE I

SLOPES OF PLOTS OF  $\log k'_M$  VERSUS LOGARITHM OF PERCHLORIC ACID ACTIVITY FOR CATIONS IN PERCHLORIC ACID ELUENTS

Data from refs. 8 and 14.

Cation	Slope	Cation	Slope	Cation	Slope	Cation	Slope
Mg <sup>2+</sup>	-1.66	Fe <sup>2+</sup>	-1.79	In <sup>3+</sup>	-2.78	Tb <sup>3+</sup>	-3.02
Ca <sup>2+</sup>	-1.87	Co <sup>2+</sup>	-1.86	Lu <sup>3+</sup>	-3.01	Gd <sup>3+</sup>	-2.99
Sr <sup>2+</sup>	-1.91	Cd <sup>2+</sup>	-2.08	Yb <sup>3+</sup>	-2.95	Eu <sup>3+</sup>	-3.01
Ba <sup>2+</sup>	-1.97	Pb <sup>2+</sup>	-2.00	Tm <sup>3+</sup>	-2.99	Sm <sup>3+</sup>	-2.97
Mn <sup>2+</sup>	-1.89	Hg <sup>2+</sup>	-1.92	Y <sup>3+</sup>	-2.95	Nd <sup>3+</sup>	-2.97
Zn <sup>2+</sup>	-1.98	Al <sup>3+</sup>	-2.88	Er <sup>3+</sup>	-2.95	Pr <sup>3+</sup>	-2.95
Ni <sup>2+</sup>	-1.87	Bi <sup>3+</sup>	-2.67	Ho <sup>3+</sup>	-3.01	Ce <sup>3+</sup>	-3.01
UO <sub>2</sub> <sup>2+</sup>	-1.96	Fe <sup>3+</sup>	-2.99	Dy <sup>3+</sup>	-3.01	La <sup>3+</sup>	-3.04
Cu <sup>2+</sup>	-1.92						

the resin surface. For example, a trivalent cation may not be able to approach closely three functional groups. This effect will tend to be most significant for large, polyvalent cations and for stationary phases of low ion-exchange capacity which therefore have a diffuse spread of functional groups. Reduction in the effective charge on the solute cation by this effect will result in slopes which are smaller than those predicted from eqn. 20.

(iii) Under conditions of relatively high eluent strength, ion-pair formation may occur between the solute cation and the sulfonic acid groups on the resin surface. The outcome of this is that the interaction between the solute and the resin will be much stronger than that expected from purely electrostatic attraction. The effective charge on the solute is therefore increased and the slope becomes greater than that predicted from eqn. 20.

Examination of the probable magnitudes of these effects in IC, where dilute eluents are used with low-capacity ion-exchange resins, suggests that effects (i) and (ii) can be expected to occur to a significant degree, especially for solute cations with a charge greater than 2. Effect (iii) is likely to be the least significant because the chromatographic conditions employed are not favourable for ion-pair formation. There is some evidence from the data of Table I to support the occurrence of effect (ii). The deviation of the experimentally observed slopes for divalent alkaline earth cations from those predicted from eqn. 20 follows the order  $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ , which is the same order for the diameters of the hydrated ions<sup>8</sup>.

It is clear from the above discussion that under conditions where the eluent contains a single type of competing cation (which is the normal situation for cation exchange), eqn. 20 is followed closely when monovalent cations are used as solutes and the eluent is dilute. Deviations may occur for solutes of higher charge, with these species requiring the use of activity corrections if meaningful estimates of effective charge are to be made.

#### *Complexing eluents with fixed-site ion-exchange columns*

Complexing ligands such as oxalate, tartrate and citrate are often used as mobile phase components for the separation of alkaline earth and transition metal cations on fixed-site cation-exchange columns. A cationic species must always be present in the eluent to preserve electroneutrality and the ion-exchange selectivity coefficient of this cation exerts a major influence on the retention mechanism which operates. When eluent cations with low selectivity coefficients (*e.g.*,  $Li^+$ ,  $Na^+$ ) are used at low concentration, elution of solutes results chiefly from the complexation (or "pulling") effect of the eluent ligand. Alternatively, when eluent cations having high selectivity coefficients (such as ethylenediammonium ions) are used, elution of solutes is achieved jointly by the complexation effect of the eluent ligand and the ion-exchange displacement (or "pushing") effect of the eluent cation.

We have examined the second of these alternatives, using eluents formed from mixtures of ethylenediamine and tartaric acid, adjusted to pH 3.2 with NaOH. The ethylenediamine concentration and the eluent pH were kept constant, whilst the value of  $\alpha_M$  was varied by changing the concentration of tartaric acid used. Linear plots of  $\log k'_M$  versus  $\log \alpha_M$  were obtained for each of the cations examined. If it is assumed that the concentration of the eluent competing cation remains constant, then eqn. 23 predicts that these plots should show a slope of 1.0 for all solutes. However, the



TABLE II

SLOPES OF  $\log k'_M$  VERSUS ( $\log \alpha_M - 2\log [\text{Na}^+]$ ) FOR DIVALENT CATIONS ELUTED FROM A FIXED-SITE CATION-EXCHANGE COLUMN

The eluents contained 1.75 mM ethylenediamine and 5–25 mM tartrate at pH 3.2.

<i>Solute</i>	<i>Slope</i>	<i>Correlation coefficient</i>
$\text{Cu}^{2+}$	1.08	1.00
$\text{Zn}^{2+}$	1.08	0.99
$\text{Co}^{2+}$	1.15	0.99
$\text{Fe}^{2+}$	1.00	0.99

experimental slopes were considerably higher, falling in the range 1.32–1.88. The chief reason for this was the presence of varying amounts of sodium ions in the different eluents, as a result of the necessity to adjust pH. These sodium ions act as competing cations in the eluent (this can be demonstrated by the elution of solute cations using sodium nitrate as eluent) and so contribute to elution of solute ions. A correction for added sodium was made by plotting  $\log k'_M$  versus ( $\log \alpha_M - 2\log [\text{Na}^+]$ ) and the slopes of these plots are shown in Table II. The results obtained are in good agreement with eqn. 23.

A similar study of the retention of trivalent cations on low-capacity cation-exchange columns using ethylenediamine–tartrate eluents at pH 4.5 obtained slopes averaging 1.2 for plots of  $\log k'_M$  versus  $\log \alpha_M$  (ref. 9). No correction was made for the presence of sodium ions in these eluents.

#### *Complexing eluents with dynamically-coated ion-interaction columns*

The above studies have established that eqns. 20 and 23 are applicable to the elution of cations from fixed-site ion-exchange columns using eluents with or without complexing agents. It is therefore interesting to apply the same retention model to the separation of cations by ion-interaction chromatography. Well-established methods exist for cation separation on  $\text{C}_{18}$  columns using eluents comprising a complexing ligand (e.g. oxalate) and an aliphatic sulfonic acid (e.g., octanesulfonic acid) as the ion-interaction reagent<sup>11</sup>.

There is some uncertainty surrounding the mechanism of separation in ion-interaction chromatography. One possible mechanism is that solute retention results from binding of ion-pairs (formed between the solute ions and the ion-interaction reagent) onto the  $\text{C}_{18}$  surface. An alternative mechanism suggests that the  $\text{C}_{18}$  surface is converted into a dynamic ion-exchanger by binding of the ion-interaction reagent and the solute is then retained by a conventional ion-exchange mechanism. The latter approach (called the dynamic ion-exchange model) can be investigated by comparing the retention behaviour obtained on fixed-site exchangers with that obtained by ion-interaction chromatography. If a dynamic ion-exchange mechanism is operative for the ion-interaction chromatographic system under study, then solute retention should be predictable from eqns. 20 and 23 and the retention mechanism will be as depicted in Fig. 1b. In this case, the eluent competing cations are the sodium ions added during pH adjustment.

We have employed eluents comprising varying concentrations of oxalate (at pH 3.4) and 2 mM octanesulfonic acid. It should be noted that these eluents contain varying amounts of sodium ion. Retention data for a range of divalent cations were obtained and plots of  $\log k'_M$  versus  $(\log \alpha_M - 2 \log [\text{Na}^+])$  were constructed. Linear plots were obtained in all cases, as indicated by the correlation coefficients listed with the slopes of these plots in Table III. It can be seen that the slopes differ markedly between ions, but all values are less than the theoretical value of 1.00 which would apply if the retention of these solutes was in accordance with eqn. 23.

A possible reason for this is that the dynamic ion-exchange capacity of the column may not have remained constant for each of the eluents examined. The experimental procedure employed involved increasing the concentration of oxalate whilst the pH and concentration of octanesulfonate were kept constant. We have already seen that the sodium concentration also varies considerably between eluents. It can be expected that the increasing ionic strength of each successive eluent would result in increased adsorption of the octanesulfonate onto the  $\text{C}_{18}$  surface as a consequence of activity effects, thereby raising the effective ion-exchange capacity of the column<sup>15</sup>. The result of this is that the observed capacity factor for each solute would be greater for the more concentrated eluents than that predicted on the assumption that ion-exchange capacity was constant. This, in turn, would lead to slopes less than those predicted from eqn. 23. Moreover, this effect would be expected to be greatest for the less-retained solute ions. The solute ions in Table III are listed in the order in which they are eluted, and it can be seen that the experimental slopes show a general increase towards the longer retained solutes.

Attempts to measure the ion-exchange capacity of the column with various eluents were unsuccessful (see below). It was therefore not possible to confirm whether the above-mentioned ion-exchange capacity effects were present to a significant degree. The results obtained in this study do not permit any firm inference to be drawn regarding the applicability of the dynamic ion-exchange retention model to the ion-interaction system under study. However, the high degree of linearity of the plots obtained (Table III) can be seen as positive evidence in support of this model.

The ion-exchange capacity of the dynamically coated column can be manipulated by changing the concentration of ion-interaction reagent in the eluent. It should

TABLE III

SLOPES OF  $\log k'_M$  VERSUS  $(\log \alpha_M - 2 \log [\text{Na}^+])$  FOR DIVALENT CATIONS IN AN ION-INTERACTION CHROMATOGRAPHIC SYSTEM

The eluents contained 2 mM octanesulfonate and 2.5–20 mM oxalate at pH 3.4.

<i>Solute</i>	<i>Slope</i>	<i>Correlation coefficient</i>
$\text{Cu}^{2+}$	0.478	1.00
$\text{Pb}^{2+}$	0.410	0.97
$\text{Zn}^{2+}$	0.490	0.96
$\text{Ni}^{2+}$	0.416	0.96
$\text{Co}^{2+}$	0.506	0.98
$\text{Cd}^{2+}$	0.648	0.98
$\text{Mn}^{2+}$	0.702	0.98

therefore be possible to investigate the effect of  $Q$  on solute retention by measuring retention data for eluents containing oxalate at constant concentration and pH, but with differing concentrations of octanesulfonic acid. The sodium ion concentration will also vary between eluents. Under these conditions, eqn. 20 can be rewritten as:

$$\log k'_M = 2\log Q - 2\log [\text{Na}^+] + \text{constant} \quad (24)$$

since the charges on the eluent and solute cations are +1 and +2, respectively. Retention data were obtained using the experimental conditions described above. Attempts were made to determine the effective ion-exchange capacity of the column for each eluent by performing breakthrough experiments with  $\text{Co}^{2+}$  and measuring the absorbance of the column effluent with a UV detector. These attempts were unsuccessful since poorly defined breakthrough curves resulted in most cases. Simple measurement of the amount of adsorbed octanesulfonate, for example using breakthrough techniques with a refractive index detector, can be used to determine the total ion-exchange capacity of the column, but the effective ion-exchange capacity may be lower because of the probability that some of the adsorbed octanesulfonate does not provide accessible ion-exchange sites. This behaviour has been observed for very hydrophobic cationic ion-interaction reagents<sup>16</sup>. However, it was evident that the ion-exchange capacity when 2 mM octanesulfonate was used in the eluent was of the order of 390  $\mu\text{equiv./g.}$  which is similar to the ion-exchange capacity of the fixed-site exchanger used in the earlier studies (450  $\mu\text{equiv./g.}$ ).

In view of the unavailability of accurate values for the ion-exchange capacity, plots of  $\log k'_M$  versus  $\log [\text{ion-interaction reagent}]$  were prepared and these are shown in Fig. 2. Capacity factors for all solute cations increased with increasing eluent concentrations of octanesulfonic acid up to 3 mM, above which a small decrease in

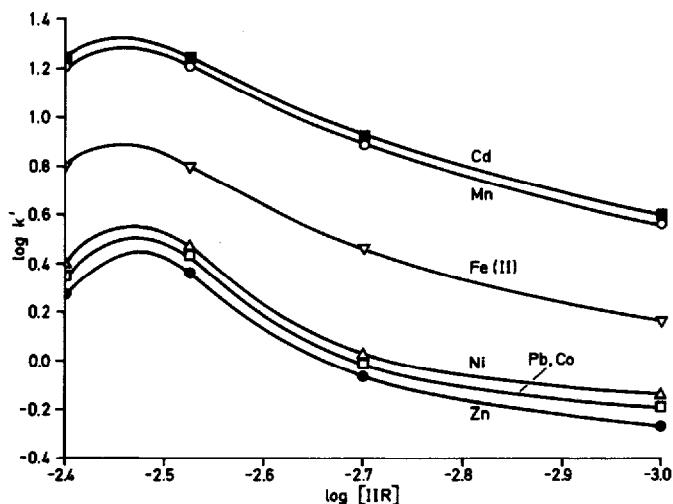


Fig. 2. Variation of solute capacity factors in an ion-interaction chromatographic system with increasing concentration of the ion-interaction reagent (octanesulfonate, IIR) in the eluent. Data are plotted in accordance with eqn. 24.

retention was observed. This behaviour can be attributed to saturation of the C<sub>18</sub> surface by the ion-interaction reagent at the higher concentration<sup>17</sup>, although other explanations, such as equilibrium effects<sup>18</sup>, micelle formation<sup>19</sup>, and decreased available hydrophobic surface area of the stationary phase<sup>20</sup> have also been proposed. The results obtained cannot be interpreted in a quantitative manner but nonetheless follow the qualitative trend predicted from eqn. 24.

## CONCLUSIONS

The general retention model derived for cations on fixed-site ion-exchange stationary phases has been shown to be valid when the eluent contains a single competing cation and also when a complexing ligand is added. The applicability of the same model was evaluated for the separation of cations using ion-interaction chromatography. The results showed qualitative agreement only with the proposed model, and this was attributed to variation of the effective ion-exchange capacity of the column. The proposed model can be used for the prediction of retention behaviour in fixed-site ion-exchange chromatographic systems and may serve as a useful basis for computer optimization techniques in cation-exchange chromatography. Studies on this aspect, together with further examination of the applicability of the retention model to ion-interaction chromatography under conditions of constant eluent ionic strength, are currently in progress.

## REFERENCES

- 1 P. R. Haddad and A. D. Sosimenko, *J. Chromatogr. Sci.*, 27 (1989) 456.
- 2 D. T. Gjerde, G. Schmuckler and J. S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
- 3 P. R. Haddad and C. E. Cowie, *J. Chromatogr.*, 303 (1984) 321.
- 4 M. J. van Os, J. Slanina, C. L. de Ligny, W. E. Hammers and J. Agterdenbos, *Anal. Chim. Acta*, 144 (1982) 73.
- 5 R. D. Rocklin, C. A. Pohl and J. A. Schibler, *J. Chromatogr.*, 411 (1987) 107.
- 6 T. B. Hoover, *Sep. Sci. Technol.*, 17 (1982) 295.
- 7 D. R. Jenke and G. K. Pagenkopf, *J. Chromatogr. Sci.*, 22 (1984) 231.
- 8 D. T. Gjerde, *J. Chromatogr.*, 439 (1988) 49.
- 9 G. J. Sevenich and J. S. Fritz, *Anal. Chem.*, 55 (1983) 12.
- 10 G. J. Sevenich and J. S. Fritz, *J. Chromatogr.*, 347 (1985) 147.
- 11 R. M. Cassidy, *Chem. Geol.*, 67 (1988) 185.
- 12 R. C. L. Foley and P. R. Haddad, *J. Chromatogr.*, 366 (1986) 13.
- 13 M. Lederer, *J. Chromatogr.*, 452 (1988) 265.
- 14 G. J. Sevenich and J. S. Fritz, *J. Chromatogr.*, 347 (1986) 361.
- 15 A. Bartha and G. Vigh, *J. Chromatogr.*, 395 (1987) 503.
- 16 P. R. Haddad and P. E. Jackson, *J. Chromatogr.*, 407 (1987) 121.
- 17 A. T. Melin, Y. Askemark, K. G. Wahlund and G. Schill, *Anal. Chem.*, 51 (1979) 976.
- 18 J. H. Knox and G. R. Laird, *J. Chromatogr.*, 122 (1976) 17.
- 19 Cs. Horváth, W. Melander, I. Molnár and P. Molnár, *Anal. Chem.*, 49 (1977) 2295.
- 20 C. T. Hung and R. B. Taylor, *J. Chromatogr.*, 202 (1980) 333.